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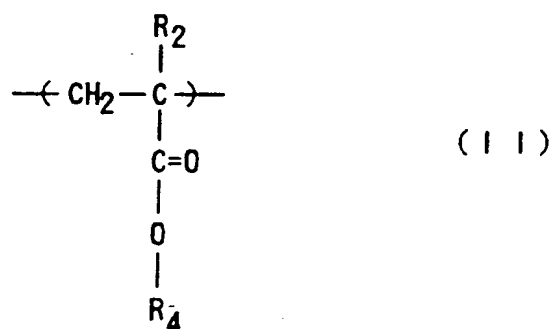
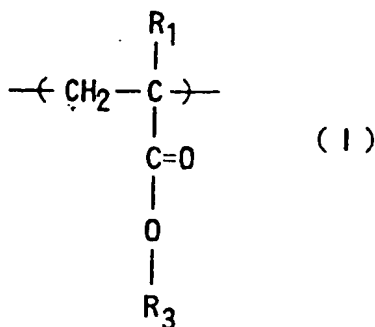
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(54) (METH)ACRYLIC ESTER COPOLYMERS AND PROCESS FOR PRODUCING THE SAME

(57) Random or block copolymers of a (meth)acrylic ester, which comprise structural units represented by general formulae (I) and (II) and have a number-average molecular weight of 1,000 to 50,000, a weight-average molecular weight (M_w) to number-average molecular weight (M_n) ratio, M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units represented by formula (I) to those represented by formula (II) of 1/9 to 9/1 (wherein R_1 and R_2 each independently represents hydrogen or methyl; R_3 represents an optionally substituted C_{7-15} alicyclic group or an alkyl group having the alicyclic group; and R_4 represents hydrogen, an optionally substituted C_{1-12} alkyl, optionally substituted C_{3-6} alicyclic or heterocyclic group, or substituted silyl group having a C_{1-8} alkyl and/or aryl group). The copolymers have each a unimodal narrow molecular weight distribution and an essential skeleton having at least one segment with a controlled structure comprising (meth)acrylic ester units each having an organic group containing a bulky alicyclic group.



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DescriptionTechnological Fields:

- 5 **[0001]** The present invention relates to narrow polydispersity (meth)acrylic ester copolymers, and, in more detail, to narrow polydispersity (meth) acrylic ester copolymers having a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (Mw) to number-average molecular weight (Mn), Mw/Mn, of 1.00 to 1.40, and an essential skeleton having at least one segment with a controlled structure comprising (meth)acrylic ester units each having an organic group containing a bulky alicyclic group, and to processes for producing the same. The copolymers
10 of this invention will meet expectations for use as materials for ArF excimer laser resists.

Background Art

- [0002]** LSI integration has become denser every year. Along with it, there has been demand for finer patterns. Photolithography by light exposure is used for fine processing. A promising candidate for next-generation technologies is excimer lithography using a KrF excimer laser for 256 Mb DRAM which needs 0.25 μm rule or an ArF excimer laser for 1Gb DRAM which needs 0.15 μm rule. A base resin to be highly transparent as a single-layer resist and excellent in dry etching resistance is essential for a material for ArF excimer laser resists. (Meth)acrylic ester copolymers that have an essential skeleton having at least one segment with a controlled structure comprising (meth)acrylic ester units each
20 having an organic group containing a bulky alicyclic group have attracted attention. Usually such base resins for resists should be copolymers produced with 2 to 4 components including other (meth)acrylic esters and/or (meth)acrylic acid, in order to improve adhesion with a substrate and control alkali solubility, in addition to the aforementioned transparency and dry etching resistance.

- [0003]** Documents, such as Japanese Patent Laid-Opened No. Hei 4-39665, Japanese Patent Laid-Opened No. Hei 5-265212 and J. Photopolym. Sci. Technol. 5 [3], 439 (1992), describe multi-component copolymers that have an essential component comprising (meth)acrylic ester units each having an organic group containing a bulky alicyclic group. However, these conventional copolymers obtained are not unimodal narrow polydispersity copolymers and have a disadvantage that the value of molecular weight distribution, Mw/Mn, is 2 to 5 and very wide. It is difficult to produce a copolymer with a controlled structure in a multi-component system using three or more components. It is also difficult
30 to produce complete block copolymers. In addition, it is necessary to remove non-reacted monomers and by-produced compounds with low molecular weight after polymerization. This is uneconomical and is another problem.

- [0004]** It is an object of this invention to provide random or block (meth) acrylic ester copolymers that have a unimodal narrow molecular weight distribution and an essential skeleton having at least one segment with a controlled structure comprising (meth)acrylic ester units each having an organic group containing a bulky alicyclic group, and processes for
35 producing the same.

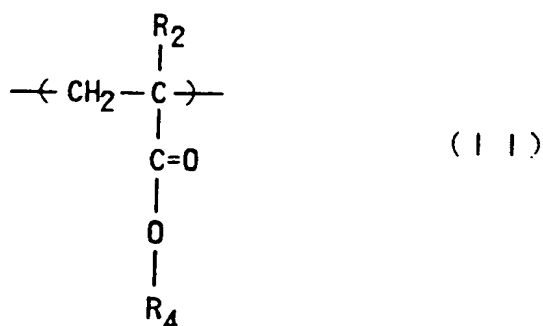
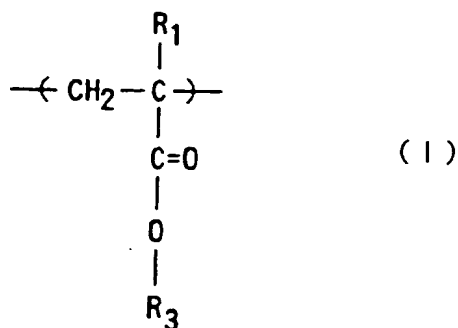
Disclosure of the Invention

- [0005]** The inventors of the present invention have made intensive investigation to achieve the object mentioned above, and have found that a (meth)acrylic ester copolymer that has a unimodal narrow molecular weight distribution and an essential skeleton having at least one segment with a controlled structure comprising (meth)acrylic ester units each having an organic group containing a bulky alicyclic group can be produced by living anion polymerization. This invention has been thus completed.

- [0006]** The present invention is directed to a narrow polydispersity (meth) acrylic ester copolymer which comprises structural units represented by Formulae (I) and (II)
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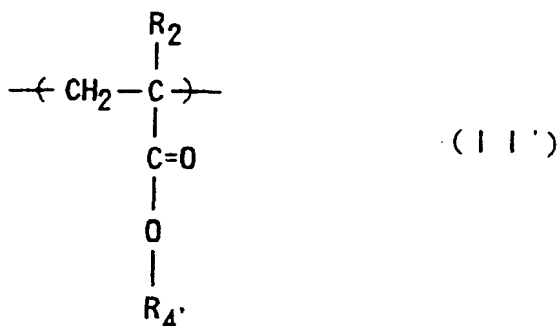
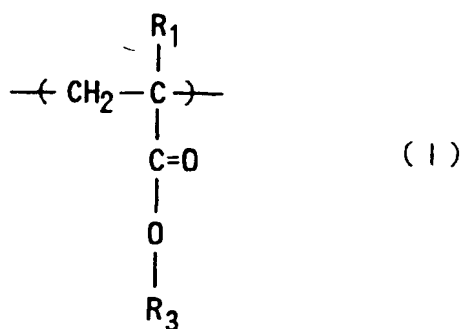
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where R_1 and R_2 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is hydrogen, an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units represented by Formula (I) to those of Formula (II) of 1/9 to 9/1. The said copolymer is a random, block or partial block copolymer.

[0007] The said copolymer is represented as follows, if it does not have a (meth)acrylic acid segment:

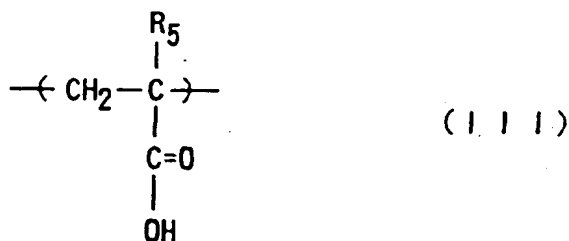
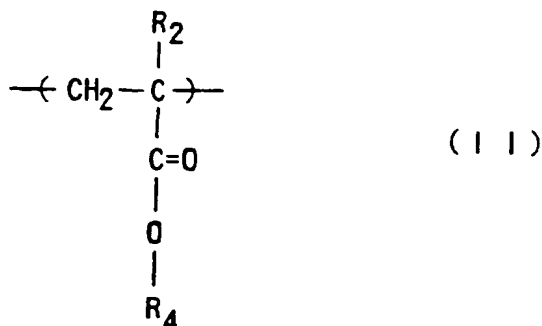
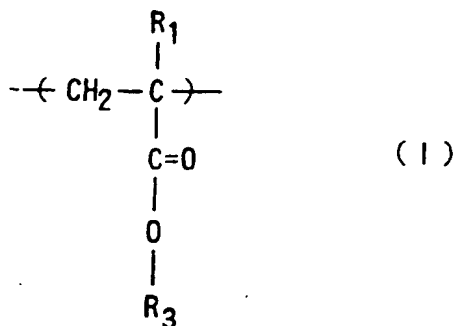
[0008] A narrow polydispersity (meth)acrylic ester copolymer which comprises structural units represented by Formulae (I) and (II)



where R_1 and R_2 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (Mw) to number-average molecular weight (Mn), Mw/Mn, of 1.00 to 1.40, and a ratio of the repeating structural units represented by Formula (I) to those of Formula (II) of 1/9 to 9/1.

[0009] The said copolymer is represented as follows, if it has a (meth) acrylic acid segment as an essential skeleton:

[0010] A narrow polydispersity (meth)acrylic ester copolymer which comprises structural units represented by Formulae (I), (II) and (III)

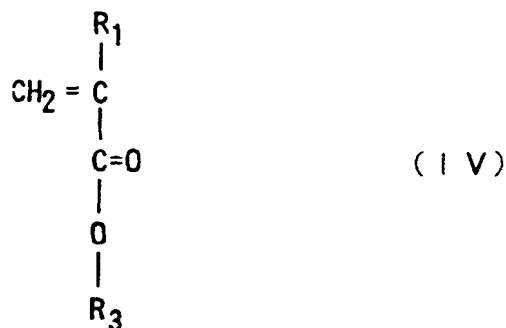


where R_1 , R_2 and R_5 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is hydrogen, an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units of Formula (I) to the total of those of Formulae (II) and (III) of 1/9 to 9/1.

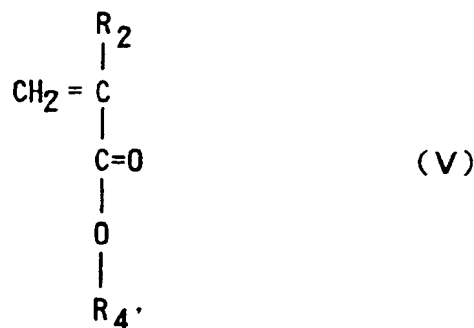
[0011] The present invention is also directed to a process for producing the said narrow polydispersity (meth)acrylic ester copolymers by living anion polymerization.

[0012] The following is a process for the said copolymer without having a (meth)acrylic acid segment:

[0013] A process for producing a narrow polydispersity (meth)acrylic ester copolymer, in which a (meth)acrylic ester of Formula (IV)



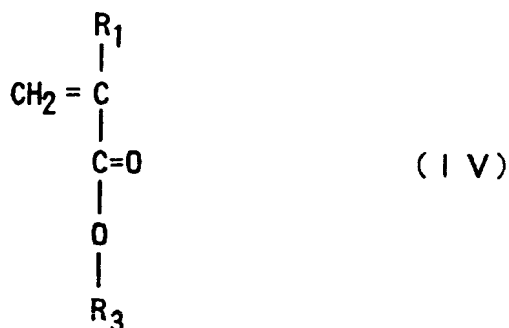
(where R_1 is hydrogen or methyl and R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group)
is copolymerized with a (meth)acrylic ester of Formula (V)



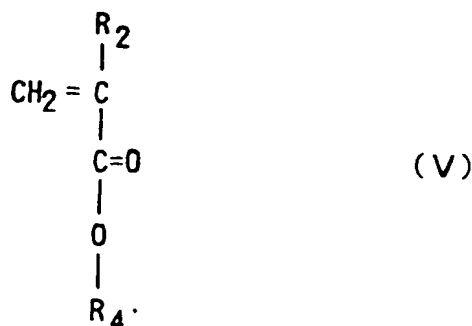
(where R_2 is each independently hydrogen or methyl and R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons)
by anion polymerization using an alkali metal or organic alkali metal as an initiator.

[0014] The following is a process for the said copolymers with a (meth) acrylic acid segment as an essential skeleton:

[0015] A process for producing a narrow polydispersity (meth)acrylic ester copolymer, in which a (meth)acrylic ester of Formula (IV)



(where R_1 is hydrogen or methyl and R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group)
is copolymerized with a (meth)acrylic ester of Formula (V)



(where R_2 is hydrogen or methyl and R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons)

by anion polymerisation using an alkali metal or organic alkali metal as an initiator, followed by the hydrolysis of part or the whole of R_4 with acidic and/or alkaline reagents to introduce a (meth)acrylic acid skeleton into the copolymer chain.

[0016] Examples of (meth)acrylic esters of Formula (IV) in this invention include 1-adamantyl acrylate, 1-adamantyl methacrylate, 2-methyl-2-adamantyl acrylate, 2-methyl-2-adamantyl methacrylate, 1-methyleneadamantyl acrylate, 1-methyleneadamantyl methacrylate, 1-ethyleneadamantyl acrylate, 1-ethyleneadamantyl methacrylate, 3,7-dimethyl-1-adamantyl acrylate, 3,7-dimethyl-1-adamantyl methacrylate, isobornyl acrylate, isobornyl methacrylate, tricyclodecanyl acrylate, tricyclodecanyl methacrylate, norbornane acrylate, norbornane methacrylate, menthyl acrylate and menthyl methacrylate. These compounds are used alone or a mixture of two or more.

[0017] In the present invention, examples of (meth)acrylic esters of Formula (V), when they have an alkyl group of 1 to 12 carbons, include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isodecyl acrylate, isodecyl methacrylate, isooctyl acrylate, isooctyl methacrylate, lauryl acrylate and lauryl methacrylate; examples of (meth)acrylic esters having an alicyclic or heterocyclic group of 3 to 6 carbons include cyclohexyl acrylate, cyclohexyl methacrylate, tetrahydrofuranyl acrylate, tetrahydrofuranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl methacrylate, 3-oxocyclohexyl acrylate, 3-oxocyclohexyl methacrylate, butyrolactone acrylate, butyrolactone methacrylate and mevalonic lactone methacrylate; and

examples of (meth)acrylic esters having a substituted silyl group include trimethylsilyl acrylate, trimethylsilyl methacrylate, isopropyl dimethylsilyl acrylate, isopropyl dimethylsilyl methacrylate, t-butyl dimethylsilyl acrylate, t-butyl dimethylsilyl methacrylate, phenyl dimethylsilyl acrylate and phenyl dimethylsilyl methacrylate.

[0018] These compounds are used alone or as a mixture of two or more.

[0019] A process for producing the copolymers of the present invention is by reacting the aforementioned (meth)acrylic esters of Formulae (IV) and (V) by anion polymerization using an alkali metal or organic alkali metal as an initiator. Usually a copolymer with a controlled structure and narrow molecular-weight distribution is obtained when polymerization is carried out in organic solvents in the atmosphere of inert gas, such as nitrogen or argon, at a temperature between -100°C and 50°C , preferably between -70°C and 0°C .

[0020] Examples of alkali metals for initiators are lithium, sodium, potassium and cesium. Alkyl, allyl and aryl compounds of the alkali metals mentioned above can be used as organic alkali metals. Examples of these compounds include ethyl lithium, n-butyl lithium, s-butyl lithium, t-butyl lithium, ethyl sodium, lithium biphenyl, lithium naphthalene, lithium triphenyl, sodium biphenyl, sodium naphthalene, sodium triphenyl, 1,1-diphenylhexyl lithium and 1,1-diphenyl-3-methylpentyl lithium.

[0021] Organic solvents used in this invention are those commonly used in anion polymerization, including aliphatic hydrocarbons such as n-hexane and n-heptane; alicyclic hydrocarbons such as cyclohexane and cyclopentane; aromatic hydrocarbons such as benzene and toluene; ethers such as diethyl ether, tetrahydrofuran and dioxane; and anisole and hexamethylphosphoramide. These are used alone or as a mixture of two or more.

[0022] As for a copolymer shape, a random copolymer in which each component is statistically distributed over a copolymer chain, partial block copolymer or complete block copolymer is synthesized, depending on how to add the aforementioned (meth)acrylic esters. For example, a random copolymer is produced by adding a mixture of compounds of the aforementioned Formulae (IV) and (V) to a reaction system for polymerization. A partial block copolymer is produced in a process that one of the compounds is aly polymerized, followed by adding a mixture of the other compounds

to continue polymerization, or part of one of the compounds is polymerized beforehand and a mixture of both compounds is added to continue polymerization. A complete block polymer is produced by adding compounds of the aforementioned Formulae (IV) and (V) one by one to a reaction system for polymerization.

[0023] According to the above processes, narrow polydispersity (meth)acrylic ester copolymers that have any number-average molecular weight in the range between 1,000 and 50,000, a ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, more preferably 1.00 to 1.30, and a ratio of repeating structural units of Formula (I) to those of Formula (II) of 1/9 to 9/1 can be produced.

[0024] A (meth)acrylic acid segment is introduced into a chain of a copolymer produced according to the aforementioned process, by hydrolysis in an organic solvent or a mixture of organic solvents including alcohols such as methanol and ethanol, ketones such as acetone and methyl ethyl ketone, cellosolves such as ethyl cellosolve and halogenated hydrocarbons such as carbon tetrachloride, in addition to the solvents exemplified in the polymerization reactions mentioned above, at a temperature between room temperature and 150° C, with a catalyst of an acidic reagent such as hydrochloric acid, hydrogen chloride gas, sulfuric acid, hydrobromic acid, 1,1,1-trifluoroacetic acid and p-toluenesulfonic acid or an alkaline reagent such as sodium hydroxide, ammonium hydroxide and tetramethyl ammonium hydroxide. In this case, only the (meth)acrylic ester skeleton represented by Formula (II') is hydrolyzed without hydrolyzing the (meth)acrylic ester of Formula (I). The degree of hydrolysis is controlled by choosing such conditions as a type of catalyst, addition amounts, reaction temperature and reaction time, for producing a target (meth)acrylic acid skeleton..

Most Preferred Embodiment

[0025] The present invention is described in more detail in reference to Examples and Comparative Examples. The scope of this invention is not, however, restricted by the following examples.

[0026] In Examples, m stands for the total number of the repeating units of the (meth)acrylic ester segment of Formula (I), n is the total number of the repeating units of the (meth)acrylic ester segment of Formula (II') and p is the total number of the repeating units of the (meth)acrylic ester segment of Formula (III).

Example 1

[0027] In a nitrogen atmosphere, 20 mmol of s-butyl lithium was added into 1000 g of tetrahydrofuran (hereinafter abbreviated as THF). 0.5 mol of 1-adamantyl methacrylate (synthesized from 1-adamantanol and methacrylic chloride and purified by distillation) was dropped over 30 minutes in stirring while keeping the temperature at -60° C. The reaction continued for another hour. The reaction completion was confirmed by gas chromatography (hereinafter abbreviated as GC). Then, 0.5 mol of t-butyl methacrylate was dropped over 30 minutes. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0028] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.5%. Measurements of the polymer by gel permeation chromatography (hereinafter abbreviated as GPC) showed that it was a narrow polydispersity polymer with $M_n = 9,100$ and $M_w/M_n = 1.15$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n = 25.1/25.3$.

[0029] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity block copolymer comprising 1-adamantyl methacrylate and t-butyl methacrylate was obtained.

Example 2

[0030] In a nitrogen atmosphere, 40 mmol of s-butyl lithium was added into 1000 g of THF. Each of 0.4 mol of 1-adamantyl methacrylate (same as that used in Example 1), 0.8 mol of methyl methacrylate and 0.8 mol of t-butyl methacrylate, in this order, was dropped into the reaction system over 30 minutes and stood for an hour, in stirring while keeping the temperature at -60° C. The copolymerization was carried out while confirming the reaction completion by GC at each stage. Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.8%.

[0031] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with $M_n = 7,100$ and $M_w/M_n = 1.20$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n = 10.0/40.0$.

[0032] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity block copolymer comprising 1-adamantyl methacrylate, methyl methacrylate and t-butyl methacrylate was obtained.

Example 3

[0033] In a nitrogen atmosphere, 10 mmol of s-butyl lithium was added into 1000 g of THF. 0.5 mol of isobornyl methacrylate (a commercial product was purified by distillation for use) was dropped over 30 minutes in stirring while keeping the temperature at -40° C. The reaction continued for another hour. The reaction completion was confirmed by GC. Then, a mixture of 0.2 mol of t-butyl acrylate and 0.2 mol of tetrahydropyranyl methacrylate was dropped over 30 minutes. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0034] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.3%. GPC measurements of the polymer showed that it was a narrow polydispersity polymer with Mn = 17,000 and Mw/Mn = 1.18. Its ¹³C-NMR showed a copolymerization ratio, m/n = 49.8/40.0.

[0035] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity partial block copolymer comprising isobornyl methacrylate, t-butyl acrylate and tetrahydropyranyl methacrylate was obtained.

Example 4

[0036] In a nitrogen atmosphere, 50 mmol of s-butyl lithium was added into 1000 g of THF. A mixture of 0.5 mol of tricyclodecanyl methacrylate (a commercial product was purified by distillation for use), 0.5 mol of t-butyl methacrylate and 0.3 mol of tetrahydropyranyl methacrylate was dropped over 30 minutes in stirring while keeping the temperature at -60° C. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0037] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a nutritious, white powder polymer. The polymerization yield to the total amount of the monomers used was 99.3%.

[0038] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with Mn = 4,680 and Mw/Mn = 1.10. Its ¹³C-NMR showed a copolymerization ratio, m/n = 10.2/15.9.

[0039] Based on the above results, it was confirmed that copolymerization was carried out as expected and a narrow polydispersity random copolymer comprising tricyclodecanyl methacrylate, t-butyl methacrylate and tetrahydropyranyl methacrylate was obtained.

Example 5

[0040] In a nitrogen atmosphere, 40 mmol of s-butyl lithium was added into 1000 g of THF. 0.5 mol of t-butyl methacrylate was dropped over 30 minutes in stirring while keeping the temperature at -60° C. The reaction continued for another hour. The reaction completion was confirmed by GC. Then, a mixture of 0.3 mol of 1-methylenadamantyl methacrylate (synthesized from 1-adamantane methanol and methacrylic chloride and purified by distillation), 0.3 mol of methyl methacrylate and 0.2 mol of 3-oxocyclohexyl methacrylate was dropped over 30 minutes. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0041] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.8%.

[0042] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with Mn = 5,280 and Mw/Mn = 1.18. Its ¹³C-NMR showed a copolymerization ratio, m/n = 7.6/25.5.

[0043] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity partial block copolymer comprising t-butyl methacrylate, 1-methylenadamantyl methacrylate, methyl methacrylate and 3-oxocyclohexyl methacrylate was obtained.

Example 6

[0044] In a nitrogen atmosphere, 10 mmol of n-butyl lithium was added into 1000 g of THF. 0.5 mol of 2-methyl-2-adamantyl methacrylate (synthesized from 2-methyl-2-adamantanol and methacrylic chloride and purified by distillation) was dropped over 30 minutes in stirring while keeping the temperature at -60° C. The reaction continued for another hour. The reaction completion was confirmed by GC. Then, 0.5 mol of t-butyl methacrylate was dropped over 30 minutes. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0045] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.8%.

[0046] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with $M_n = 19,170$ and $M_w/M_n = 1.13$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n = 51.0/50.8$.

[0047] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity block copolymer comprising 2-methyl-2-adamantyl methacrylate and t-butyl methacrylate was obtained.

Example 7

[0048] 40 mmol of n-butyl lithium and 42 mmol of 1,1-diphenyl ethylene were added into 1000 g of THF in a nitrogen atmosphere in stirring while keeping the temperature at -40°C , to give 1,1-diphenylhexyl lithium. A mixture of 0.5 mol of 1-adamantyl acrylate (synthesized from 1-adamantanol and acrylic chloride and purified by distillation), 0.3 mol of t-butyl methacrylate, 0.3 mol of cyclohexyl methacrylate and 0.3 mol of methyl acrylate was dropped into the reaction system over 30 minutes. The reaction continued for another hour. The reaction completion was confirmed by GC.

[0049] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60°C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 98.2%.

[0050] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with $M_n = 5,900$ and $M_w/M_n = 1.25$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n = 12.5/22.5$.

[0051] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity random copolymer comprising 1-adamantyl acrylate, t-butyl methacrylate, cyclohexyl methacrylate and methyl acrylate was obtained.

Example 8

[0052] In a nitrogen atmosphere, 20 mmol of s-butyl lithium was added. A mixture of 0.5 mol of 2-methyl-2-adamantyl methacrylate, 0.2 mol of t-butyldimethylsilyl methacrylate (synthesized from 1-butyldimethylsilyl chloride and methacrylic acid and purified by distillation) and 0.3 mol of t-butyl methacrylate was dropped over 30 minutes in stirring while keeping the temperature at -60°C . The reaction continued for another hour. The reaction completion was confirmed by GC.

[0053] Methanol was added into the reaction system to terminate the reaction. The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60°C for 5 hours under reduced pressure to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 99.0%.

[0054] GPC measurements of the polymer showed that it was a narrow polydispersity polymer with $M_n = 10,100$ and $M_w/M_n = 1.20$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n = 25.1/25.0$.

[0055] Based on the above results, it was confirmed that copolymerization was carried out as designed and a narrow polydispersity random copolymer comprising 2-methyl-2-adamantyl methacrylate, t-butyldimethylsilyl methacrylate and t-butyl methacrylate was obtained.

Example 9

[0056] 10 g of the polymer obtained in Example 1 was dissolved in a mixed solvent of toluene/ethanol (2/1) to make a 20% solution and 1 g of concentrated hydrochloric acid was added to react at 65°C for an hour. The reaction solution was poured into a large amount of water. The polymer deposited was filtrated, washed and dried at 70°C for 5 hours to give 9.7 g of white powder polymer. GPC measurements of the polymer showed $M_n = 9,020$ and $M_w/M_n = 1.15$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n/p = 25.1/21.8/3.6$. The acid value was 22.3.

[0057] Based on the above results, it was confirmed that a narrow polydispersity partial block copolymer comprising 1-adamantyl methacrylate, t-butyl methacrylate and methacrylic acid was obtained.

Example 10

[0058] 10 g of the polymer obtained in Example 3 was dissolved in THF to make a 20% solution and 0.2 g of p-toluenesulfonic acid was added to react at 40°C for an hour. It was confirmed by ^1H -NMR that the tetrahydropyranyl group was completely eliminated. The reaction solution was poured into a large amount of water. The polymer deposited was filtrated, washed and dried at 60°C for 5 hours to give 9.7 g of white powder polymer.

[0059] GPC measurements of the polymer showed $M_n = 15,880$ and $M_w/M_n = 1.18$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n/p = 50.0/32.1/7.7$. The acid value was 27.1.

[0060] Based on the above results, it was confirmed that a narrow polydispersity partial block copolymer comprising isobornyl methacrylate, t-butyl acrylate and methacrylic acid was obtained.

Example 11

[0061] 10 g of the polymer obtained in Example 8 was dissolved in THF to make a 10% solution and a few drops of 2N-hydrochloric acid was added to react at room temperature for 3 hours. It was confirmed by ^1H -NMR that the t-butyldimethylsilyl group was completely eliminated. The reaction solution was poured into a large amount of water. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours under reduced pressure to give 8.7 g of white powder polymer. GPC measurements of the polymer showed $M_n = 8,860$ and $M_w/M_n = 1.20$. Its ^{13}C -NMR showed a copolymerization ratio, $m/n/p = 25.1/15.0/10.0$. The acid value was 63.2.

[0062] Based on the above results, it was confirmed that a narrow polydispersity random copolymer comprising 2-methyl-2-adamantyl methacrylate, t-butyl methacrylate and methacrylic acid was obtained.

Comparative Example 1

[0063] Into 100 g of toluene were added 11 mmol of azobisisobutyronitrile (hereinafter abbreviated as AIBN) as a radical initiator, 0.1 mol of 1-adamantyl methacrylate and 0.1 mol of t-butyl methacrylate in a nitrogen atmosphere, and polymerized in stirring at 65° C for 5 hours. 5 mmol of AIBN was added. Temperature was raised to 80° C to carry on the reaction for 3 hours and further an hour at 95° C.

[0064] The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 91.3%.

[0065] GPC measurements of the polymer showed $M_n = 8,800$, $M_w/M_n = 2.8$, multi-peaks and a wide molecular-weight distribution.

Comparative Example 2

[0066] Into 100 g of toluene were added 5 mmol of AIBN, 0.1 mol of 1-adamantyl methacrylate, 0.1 mol of methyl methacrylate and 0.1 mol of t-butyl methacrylate in a nitrogen atmosphere and radical polymerization was carried out as did in Comparative Example 1.

[0067] The reaction solution was fractionally purified twice with methanol/water and poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 82.7%.

[0068] GPC measurements of the polymer showed $M_n = 20,100$, $M_w/M_n = 1.6$ and a wide molecular-weight distribution with a shoulder at the side of low molecular weight.

Comparative Example 3

[0069] Into 100 g of toluene were added 12 mmol of AIBN and 0.2 mol of isobornyl methacrylate in a nitrogen atmosphere, and polymerized in stirring at 65° C for 5 hours. 0.1 mol of t-butyl methacrylate was added to continue the reaction for 5 hours. 4 mmol of AIBN was further added. Temperature was raised to 80° C to carry on the reaction for 3 hours and further an hour at 95° C.

[0070] Non-reacted monomers and compounds with low molecular weight were removed from the reaction solution by fractional purification with methanol/water. Volatile matter was then distilled out under reduced pressure to give a polymer.

[0071] GPC measurements of the polymer showed $M_w/M_n = 4.8$ and multi-peaks. Components in each eluate from fractional GPC were measured by ^1H -NMR. The obtained polymer was a mixture of homopolymers of individual components and copolymers with irregular compositions. It was thus confirmed that the target block copolymer was not produced.

Comparative Example 4

[0072] Into 100 g of toluene were added 15 mmol of azobisisobutyronitrile (hereinafter abbreviated as AIBN) as a radical initiator, 0.1 mol of 1-adamantyl methacrylate, 0.1 mol of t-butyl methacrylate and 0.1 mol of methacrylic acid in a nitrogen atmosphere, and polymerized in stirring at 65° C for 5 hours. 0.3 mmol of AIBN was added. Temperature was raised to 80° C to carry on the reaction for 3 hours and further an hour at 95° C.

[0073] The reaction solution was poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer. The polymerization yield to the total amount of the monomers used was 92.3%.

[0074] GPC measurements of the polymer showed $M_n = 9,200$, $M_w/M_n = 3.1$, multi-peaks and a wide molecular-

weight distribution.

Comparative Example 5

5 [0075] Into 100 g of toluene were added 5 mmol of AIBN, 0.1 mol of 1-adamantyl methacrylate, 0.1 mol of methyl methacrylate, 0.1 mol of t-butyl methacrylate and 0.1 mol of acrylic acid in a nitrogen atmosphere and radical polymerization was carried out as did in Comparative Example 1.

[0076] The reaction solution was fractionally purified twice with methanol/water and poured into a large amount of methanol. The polymer deposited was filtrated, washed and dried at 60° C for 5 hours to give a white powder polymer.
10 The polymerization yield to the total amount of the monomers used was 81.5%.

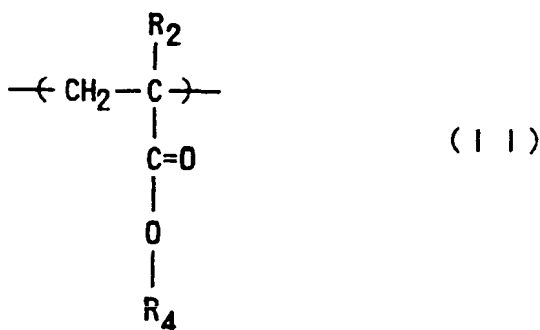
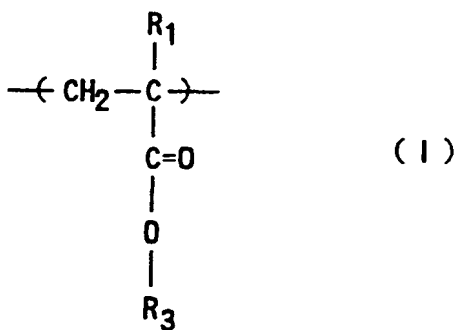
[0077] GPC measurements of the polymer showed $M_n = 23,100$, $M_w/M_n = 1.7$ and a wide molecular-weight distribution with a shoulder at the side of low molecular weight.

Industrial Use

15 [0078] The present invention provides narrow polydispersity random, block or partial block copolymers of (meth)acrylic esters, which are expected to be used as materials for ArF excimer laser resists. The copolymers have a unimodal narrow molecular-weight distribution and an essential skeleton having at least one segment with a controlled structure comprising (meth) acrylic ester units each having an organic group containing a bulky alicyclic group.
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Claims

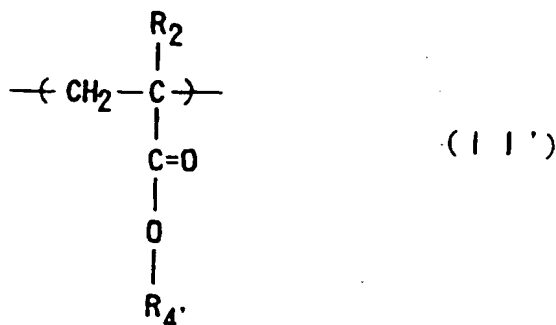
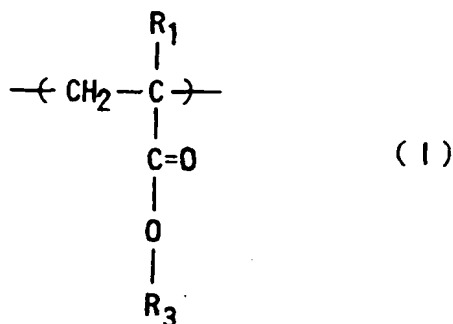
1. A narrow polydispersity (meth)acrylic ester copolymer which comprises structural units represented by Formulae (I) and (II)



where R_1 and R_2 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is hydrogen, an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units represented by Formula (I) to those
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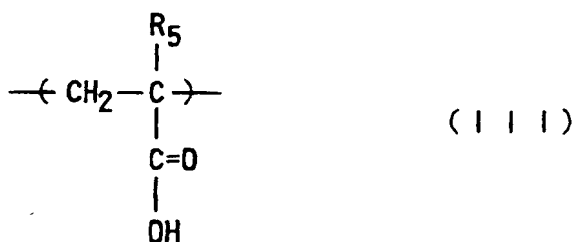
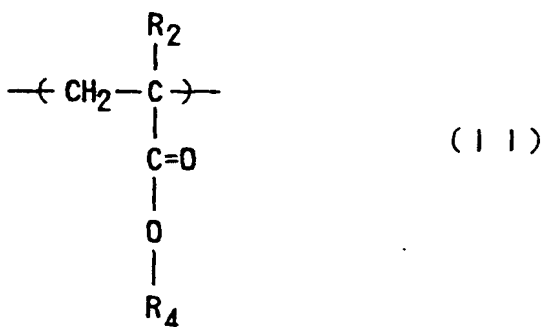
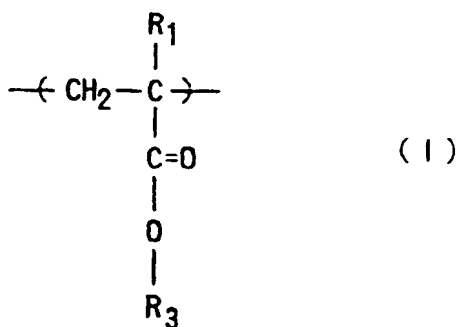
of Formula (II) of 1/9 to 9/1.

2. A narrow polydispersity (meth)acrylic ester copolymer according to Claim 1, which comprises structural units represented by Formulae (I) and (II')



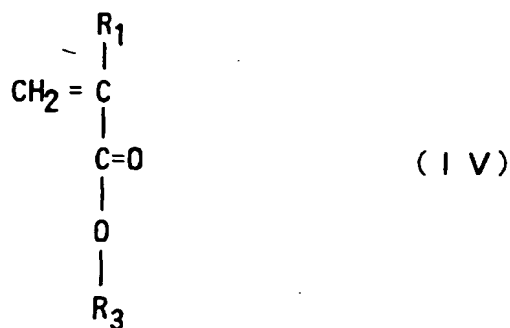
where R_1 and R_2 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units represented by Formula (I) to those of Formula (II') of 1/9 to 9/1.

3. A narrow polydispersity (meth)acrylic ester copolymer according to Claim 1, which comprises structural units represented by Formulae (I), (II) and (III)

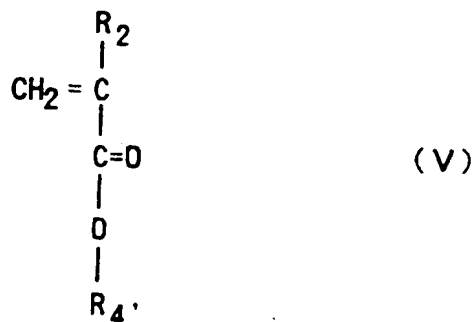


where R_1 , R_2 and R_5 are each independently hydrogen or methyl; R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group; and R_4 is hydrogen, an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons, and which has a number-average molecular weight of 1,000 to 50,000, a ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n), M_w/M_n , of 1.00 to 1.40, and a ratio of the repeating structural units of Formula (I) to the total of those of Formulae (II) and (III) of 1/9 to 9/1.

4. A narrow polydispersity (meth)acrylic ester copolymer according to Claims 1 to 3, in which the copolymer is a random copolymer.
5. A narrow polydispersity (meth)acrylic ester copolymer according to Claims 1 to 3, in which the copolymer is a block copolymer.
6. A narrow polydispersity (meth)acrylic ester copolymer according to Claims 1 to 3, in which the copolymer is a partial block copolymer.
7. A process for producing a narrow polydispersity (meth)acrylic ester copolymer according to Claim 2, in which a (meth)acrylic ester of Formula (IV)

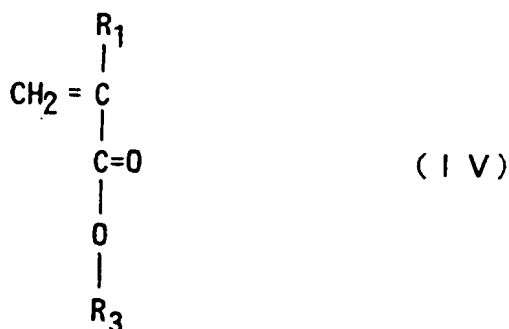


(where R_1 is hydrogen or methyl, R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group) is copolymerized with a (meth)acrylic ester of Formula (V)

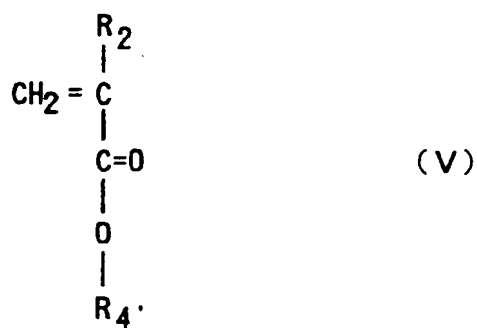


(where R_2 is each independently hydrogen or methyl, R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons), by anion-polymerization using an alkali metal or organic alkali metal as an initiator.

8. A process for producing a narrow polydispersity (meth)acrylic ester copolymer according to Claim 3, in which a (meth)acrylic ester of Formula (IV)



(where R_1 is hydrogen or methyl, R_3 is an optionally substituted alicyclic group having 7 to 15 carbons or an alkyl group having the said alicyclic group) is copolymerized with a (meth)acrylic ester of Formula (V)



(where R_2 is hydrogen or methyl, R_4 is an optionally substituted alkyl group having 1 to 12 carbons, an optionally substituted alicyclic or heterocyclic group having 3 to 6 carbons or a substituted silyl group having an alkyl and/or aryl group of 1 to 8 carbons),

by anion polymerization using an alkali metal or organic alkali metal as an initiator, followed by the hydrolysis of part or the whole of R_4 with acidic and/or alkaline reagents to introduce a (meth)acrylic acid skeleton into the copolymer chain.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04509

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁶ C08F220/12, 220/04, 8/12, 297/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁶ C08F220/04-220/30, 8/12, 297/02, 20/04-20/30, G03F7/004, 039, H01L21/027, 30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | JP, 7-120927, A (Fujitsu Ltd.), May 12, 1995 (12. 05. 95), Claim 1 ; Par. Nos. [0027] to [0039], [0087] to [0098] (Family: none) | 1, 2 4-7 |
| Y | JP, 4-39665, A (Fujitsu Ltd.), February 10, 1992 (10. 02. 92), Claim 1 ; page 2, upper right column to page 4, upper right column, Line 15 (Family: none) | 1, 2 4-7 |
| Y | JP, 5-265212, A (Fujitsu Ltd.), October 15, 1993 (15. 10. 93), Claim 1, Par. Nos. [0007] to [0008], [0017] to [0025] (Family: none) | 1, 2 4-7 |
| Y | JP, 8-123025, A (Hitachi Chemical Co., Ltd.), May 17, 1996 (17. 05. 96), Claims 1 to 7 ; Par. Nos. [0007] to [0020], [0030] to [0033], [0047] (Family: none) | 1, 2 4-7 |

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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| "P" document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search
February 25, 1998 (25. 02. 98)Date of mailing of the international search report
March 10, 1998 (10. 03. 98)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04509

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | JP, 6-266099, A (Hitachi, Ltd.), September 22, 1994 (22. 09. 94), Claims 1 to 14, Par. Nos. [0017] to [0024] (Family: none) | 1, 2 4-7 |
| Y | JP, 6-256410, A (Toyota Motor Corp., and two others), September 13, 1994 (13. 09. 94), Claim 1, Par. Nos. [0002] to [0020] (Family: none) | 1, 2 4-7 |
| Y | JP, 4-173805, A (Toa Gosei Co., Ltd.), June 22, 1992 (22. 06. 92), Claim 1 ; page 1, lower left column, 5th line from the bottom to lower right column, line 2 ; page 2, lower left column, line 11 to page 3, lower right column, last line (Family: none) | 1, 2 4-7 |
| Y | JP, 63-277218, A (Toppan Printing Co., Ltd.), November 15, 1988 (15. 11. 88), Claim 1 ; page 1, upper right column, lines 2 to 11 ; page 3, lower right column, line 1 to page 5, lower left column, last line (Family: none) | 1, 2 4-7 |
| Y | JP, 61-176617, A (Mitsubishi Rayon Co., Ltd.), August 8, 1986 (08. 08. 86), Claims 1, 2 ; page 3, lower left column, line 2 to page 4, upper left column, line 3 ; page 5, upper left column, line 1 to page 6, lower right column, line 9 (Family: none) | 1, 2 4-7 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)